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Low-Field CIDNP in Intramicellar Radical Disproportionation. Violation of Equivalency in *J*-Coupled Nuclear Spin Systems

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Observations of chemically induced dynamic nuclear polarization in low magnetic fields are often complicated by a transfer of samples from the laboratory field to the high magnetic field of the spectrometer. Effects of such transfer are analyzed, and theoretical predictions are compared to the results on low-field CIDNP in strongly coupled protons of styrene, a product of geminate disproportionation in the pair of *sec*-phenethyl and phenacyl radicals. Selective deuteration was used to decouple these protons and analyze redistribution of polarization formed in the course of disproportionation. A violation of magnetic equivalency in the protons constituting the methyl group in the precursor *sec*-phenethyl radical was observed. Possible origins of this phenomenon are discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Chemically induced dynamic nuclear polarization (CIDNP) is a common phenomenon in photoreactions involving radical pairs (RP) (*1, 2*). Typically, such pairs are generated in the triplet state and recombine from the singlet state. Consequently, the geminate reaction must be preceded by intersystem crossing in the pair. The latter is influenced by Zeeman interaction of radicals with the external magnetic field and hyperfine interactions (hfi) of nuclear and electron spins. Since hfi accelerates triplet-to-singlet conversion in some nuclear subensembles faster than in others, yields of reaction products depend on the nuclear spin configuration. This dependence causes characteristic non-Boltzmann populations of nuclear spin states in the reaction products.

In low fields, the energy gap between triplet levels of the pair is comparable with hyperfine coupling constants in the radicals, and transitions with simultaneous flip of nuclear and electron spins are very efficient (*1, 2*). In high fields (>0.1 T) these transitions are much slower and do not induce significant nuclear polarization over the lifetime of the pair. Thus, nuclear polarization generated in low fields is stronger than that generated in high fields (*3*). Unfortunately, an enhancement of polarization in low fields is coupled with extreme difficulty of detection (*2*). Indeed, insufficient spectral resolution in low fields precludes observation of the lines from different protons. This obstacle may be avoided by use of transfer techniques. Typically, a low-field CIDNP experiment includes two steps: (i) formation of polarization in the laboratory field (H_{lab}), and (ii) transfer of the sample to the high field of the spectrometer (H_{sp}), in which the NMR signals are measured (*1, 2*). The alternative method, field switching (*2, 4*), is presently out of practice since it cannot be performed with spectrometers equipped with superconducting magnets.

Evidently, the transfer should be fast so the polarization is not destroyed by longitudinal relaxation. Technically, the transfer is carried out either with a flow system or by shooting sample cells inside the cavity immediately after the completion of photolysis. Transfer times as short as 0.1 s may be achieved with these methods (*2*). Apart from low-field CIDNP, the sample transfer techniques are employed in some other experiments on chemical generation of nuclear polarization, such as stimulated nuclear polarization (*5*) and NMR-detected EPR (*6*). The very method of detection poses two questions: (i) What polarization is measured with these techniques, and (ii) how does the transfer affect the polarization? In this paper we address these questions both theoretically and experimentally.

EFFECTS OF THE SAMPLE TRANSFER IN *J*-COUPLED SPIN SYSTEMS

Formulation of the problem. Generally, nuclear spin polarization may be divided into two contributions: the so-called net polarization and the multiplet polarization (*1–3*). By use of $\pi/2$ pulses or by adding together free-induction-decay curves obtained with pulse flip angles θ and $(\pi - \theta)$, it is possible to remove multiplet polarization from spectra recorded with Fourier-transform NMR (*7, 8*). Hereafter, it will be supposed that nuclear polarization is measured in this fashion. Neglecting cross relaxation and assuming the same transverse relaxation times for each line of a given

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subspectrum associated with a nucleus k, we obtain $L_k = 2 \sum_k m_{kz}(i)P_i$, where L_k is the polarization of all the lines of kth multiplet, P_i is the population of the ith nuclear spin state, and $m_{kz}(i)$ is the projection of the kth nuclear spin on the magnetic field (z axis of the laboratory frame). Polarizations L_k may be easily found if populations P_i are known. That, however, requires some information on how the nuclear spin system is transferred from the low field to the high field. If this transfer is slow ("adiabatic transfer"), a population $\tilde{P}_\sigma$ of a given low-field nuclear spin state $|\sigma\rangle$ is transferred to that state $|i\rangle$ of the high field with which σ correlates: if $|\sigma\rangle \rightarrow |i\rangle$, then $\tilde{P}_\sigma \rightarrow P_i$. In the limit of very rapid transfer ("nonadiabatic transfer"), $P_i = \sum_\sigma |\langle\sigma|i\rangle|^2 \tilde{P}_\sigma$. In reality the transfer is neither adiabatic nor nonadiabatic. A degree of adiabaticity may be expressed in terms of a Messiah parameter M. If $M \gg 1$ the transfer is adiabatic; if $M \ll 1$ it is nonadiabatic (*9*).

A correlation between the low-field states $|\sigma\rangle$ and the high-field states $|i\rangle$ may be readily found, taking into account that in the course of the transfer only one parameter (the external magnetic field) changes and, according to the well-known Wigner rule, in the absence of internal symmetries nuclear spin terms do not cross (*9*). Although the field may change direction and there may be a region where no field besides the earth's magnetic field ($\sim 0.5g$) is present, unless the intermediate magnetic field is greater than nuclear spin–spin coupling constants, J_{ab} (which are $< 0.05g$), these terms do not cross. Consequently, it is the order of spin levels which determines what low-field state $|\sigma\rangle$ correlates with a given high-field state $|i\rangle$.

This situation is dramatically complicated if the transfer is not adiabatic. Indeed, in some intermediate fields, the nuclear states may be very close energetically. If the system passes through such a region very rapidly, the populations of spin states are mixed. These nonadiabatic transfers may occur each time a difference $\Delta\nu_{ab}$ in the Larmor frequencies of two coupled nuclei A and B is close to their coupling constant J_{ab}. Adiabaticity of such transfers may be estimated either with Fermi's golden rule (for funnels) or the Landau–Zener formula (for linear quasi-intersections) (*9*).

Estimates of adiabaticity for nearly parallel nuclear terms have been done by Kaptein (*10*). Following Ref. (*10*), let us introduce the transfer time $\tau = |H_{sp} - H_{lab}|/v$, where v is the rate of increase in the magnetic field during the transfer. Let us further assume that in a certain intermediate field $\Delta\nu_{ab} \sim J_{ab}$. We may suppose that the energy gap between coupled terms has the same order of magnitude as J_{ab}. Applying Fermi's rule we obtain $\tau \sim (\pi|J_{ab}|)^{-1}$ for the minimum time of *adiabatic* transfer (*11*). As the formula indicates, it is very unlikely that all these transfers are adiabatic: in the multinuclear systems, some protons are weakly coupled. More rigorous consideration shows that many avoided intersections of nuclear terms are linear and Fermi's rule is not applicable. A Landau–Zener estimation of transfer probabilities in these regions typically yields $M \sim (2\text{–}5)/v$ T/s. With $H_{sp} \sim 2$ T and $\tau \sim 0.5\text{–}2$ s, this estimate gives $M \sim 0.5\text{–}5$. Thus, the transfers are marginally adiabatic.

Transfer in the AB system. The effects of adiabatic transfer may be illustrated with a system of two coupled protons (AB system). The nuclear spin Hamiltonian $\mathscr{H}_N$ of this system is given by

$$\mathscr{H}_N = \nu_a I_{az} + \nu_b I_{bz} + J I_a I_b, \qquad [1]$$

where J is the spin–spin coupling constant, $\nu_{a,b} = \gamma_N H_{lab}(1 - \delta_{a,b})$ are Larmor frequencies of the nuclei, $\delta_{a,b}$ are their chemical shifts, and γ_N (<0) is the nuclear gyromagnetic ratio. Eigenvectors of $\mathscr{H}_N$ are $|\tilde{1}\rangle = |1\rangle = |\alpha\alpha\rangle$, $|\tilde{2}\rangle = \cos\chi|2\rangle + \sin\chi|3\rangle$, $|\tilde{3}\rangle = \sin\chi|2\rangle + \cos\chi\,|3\rangle$, and $|\tilde{4}\rangle = |4\rangle = |\beta\beta\rangle$, where $|2\rangle = |\alpha\beta\rangle$ and $|3\rangle = |\beta\alpha\rangle$ and $\tan\chi = J/\Delta\nu$; $\Delta\nu = \nu_a - \nu_b$ (Fig. 1). After some algebra we obtain

$$\begin{aligned} L_{a,b} &= P_1 - P_4 \pm (P_2 - P_3) \\ &= \tilde{P}_{\tilde{1}} - \tilde{P}_{\tilde{2}} \pm (|\Delta\nu|/D)^\mu[\tilde{P}_{\tilde{2}} - \tilde{P}_{\tilde{3}}], \end{aligned} \qquad [2]$$

where $\mu = 0$ for adiabatic and $\mu = 1$ for nonadiabatic transfer; $D = (\Delta\nu^2 + J^2)^{1/2}$ is the frequency of $|2\rangle \rightarrow |3\rangle$ transitions.

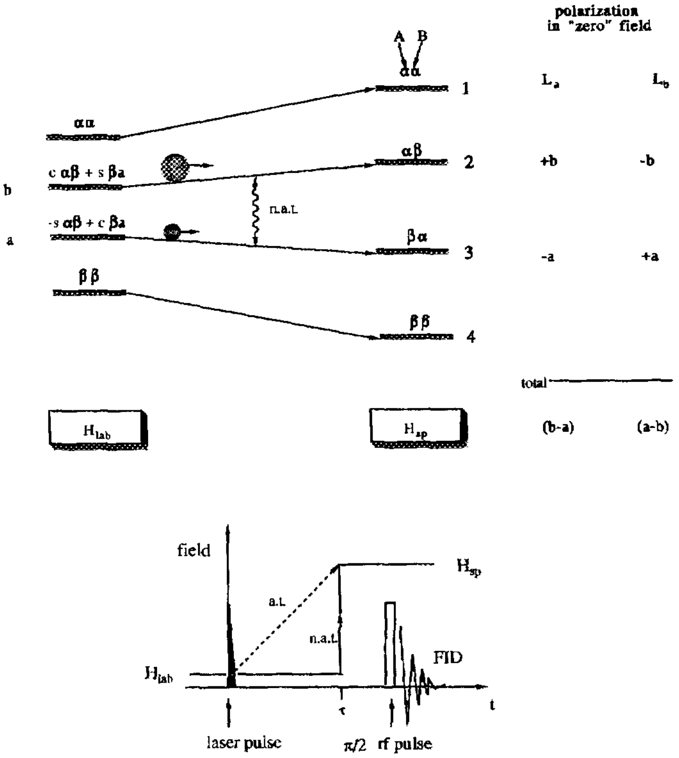

FIG. 1. (Top) Correlation diagram between low-field and high-field states for a nuclear AB system with $\delta_a > \delta_b$ and $J > 0$; $c = \cos\chi$, $s = \sin\chi$. (Bottom) Visualization of the low-field CIDNP experiment for adiabatic (a.t.) and nonadiabatic (n.a.t.) transfers.

Introducing a density matrix ρ of the nuclear spin system in low field we obtain (with the relaxation factor $\xi = 1$)

$$L_{a,b} = \rho_{11} - \rho_{44} + \xi(|\Delta\nu|/D)^{\mu} \times \{|\Delta\nu|/D(\rho_{22} - \rho_{33}) + J/D \operatorname{Re} \rho_{23}\}. \quad [3]$$

Equation [3] indicates that at $\Delta\nu \ll J$, polarizations $L_{a,b}$ are *not* equal to projections of the nuclear spins on the laboratory field (as is often assumed in the literature). This conclusion is correct whether the transfer is adiabatic or nonadiabatic. Using the cage model of a radical pair (*1*) and supposing that the lifetime of the pair is very short, we obtain the analytical expressions.

$$L_{a,b} \propto \Delta\omega(A_a + A_b) + \xi \operatorname{sgn}(\Delta\nu)(|\Delta\nu|/D)^{\mu} D^{-1} \times \{\Delta\omega\Delta\nu(A_a - A_b) + JA_aA_b\}, \quad [4]$$

where $\Delta\omega = (g_1 - g_2)\mu_B H_{lab}$ is the difference in Larmor frequencies of the radicals (it was assumed that the pair is triplet-born and that both nuclei belong to the same radical with g factor g_1). In zero field, H_0 is sufficiently weak to neglect Zeeman interactions in the radical pair and the difference in the chemical shifts of the nuclei ($\Delta\omega \approx 0$ and $\Delta\nu \ll J$), but is sufficiently high to decouple nuclear terms ($\nu \gg J$); the sign of polarization transferred adiabatically is given by

$$\operatorname{sgn}(L_{a,b}) = \pm \operatorname{sgn}(A_aA_b)\operatorname{sgn}(J)\operatorname{sgn}(\delta_a - \delta_b) \quad [5]$$

(the positive sign corresponds to the absorption). Equation [5] predicts the so-called "zero-field multiplet effect" (*11*), which was indeed observed by Ward and Lawler with slow-passage NMR (*12*). Of note, this multiplet effect cannot be eliminated by application of $\pi/2$ pulses. In the case of nonadiabatic transfer, nuclear polarization in zero field is zero. According to Eq. [5], in the field where $\Delta\nu \ll J$, $L_a \approx L_b$ in the case of nonadiabatic transfer and $L_a \approx -L_b$ in the case of adiabatic transfer.

Net CIDNP formed in the high field has a remarkable feature: protons magnetically equivalent in the radicals have equal polarizations. Of course, nuclear spin relaxation may destroy this equivalency. However, it may be expected that the formerly equivalent protons would exhibit similar field dependences of CIDNP. Contrary to these expectations, even this residual equivalency will be violated if the protons are coupled and the transfer is adiabatic [see also Ref. (*13*)].

ABC system. In zero-field H_0, the spin Hamiltonian $\mathscr{H}_N$ of three coupled protons may be approximated by $\mathscr{H}_N = \nu_0(I_{az} + I_{bz} + {}_{cz}) + (J_{ab}I_aI_b + J_{bc}I_bI_c + J_{ca}I_cI_a)$, where $\nu_0 \gg I_{ij}$. In zero field, both the spin Hamiltonian of the radical pair and the second term in $\mathscr{H}_N$ commute with the operator $I_{ax}I_{bx}I_{cx}$. The symmetry allows a correlation diagram between the nuclear states $|\sigma\rangle$ and $|i\rangle$ to be drawn without diagonalization of $\mathscr{H}_N$. Only six states with projection M_z of the overall spin $M_z = \pm\frac{1}{2}$ contribute to the adiabatically transferred polarization. Let us denote populations of the higher, middle, and lower levels of each subtriplet as c, b, and a, respectively. A simple calculation (Fig. 2) shows that at $\delta_a > \delta_b > \delta_c$, $L_a = 2(c - a)$, $L_b = 0$, and $L_c = -L_a$. The phase of polarization L_a may be found using the cage model; this calculation is very tedious and we report the final result in the Appendix. The sign of L_a is a complex function of hfi and coupling constants. Remarkably, even in the situation when $J_{ab} \gg J_{bc}$ and $J_{ab} \gg J_{ca}$, polarizations given by Eqs. [5] and [A1] may be opposite in sign: even small coupling of nuclei A and B with C changes the order of spin terms in zero field. Thus, in very low field, the separation of protons into smaller subensembles could produce a misleading result. It is also interesting to consider what happens to the polarizations if the transfer is nonadiabatic for a couple or two neighboring terms. It may be shown that L_b in the zero field is always nonzero in this case.

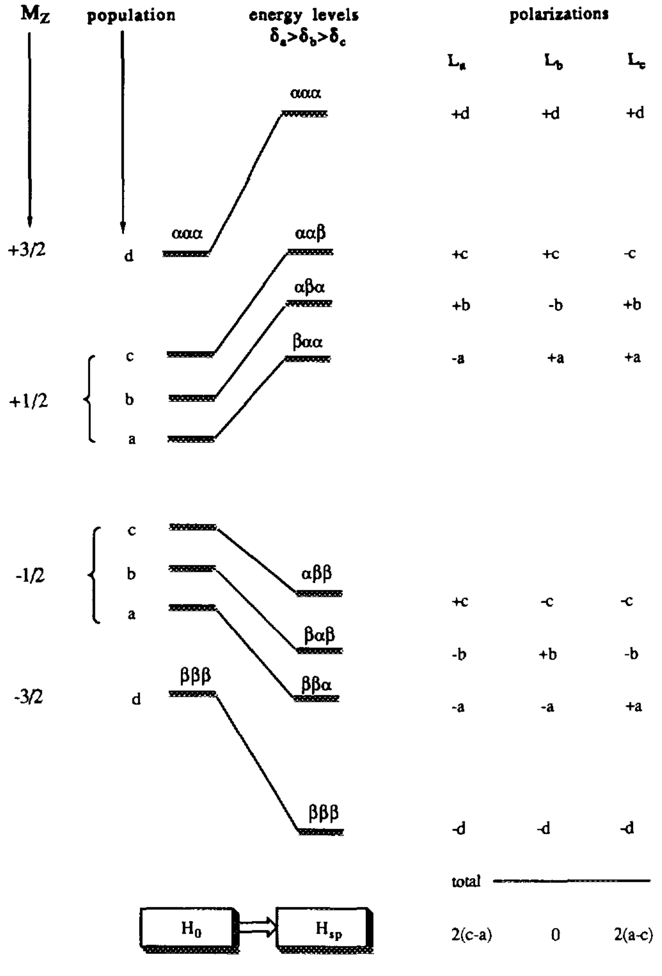

FIG. 2. Correlation between "zero"-field and high-field states in a system of three coupled protons.

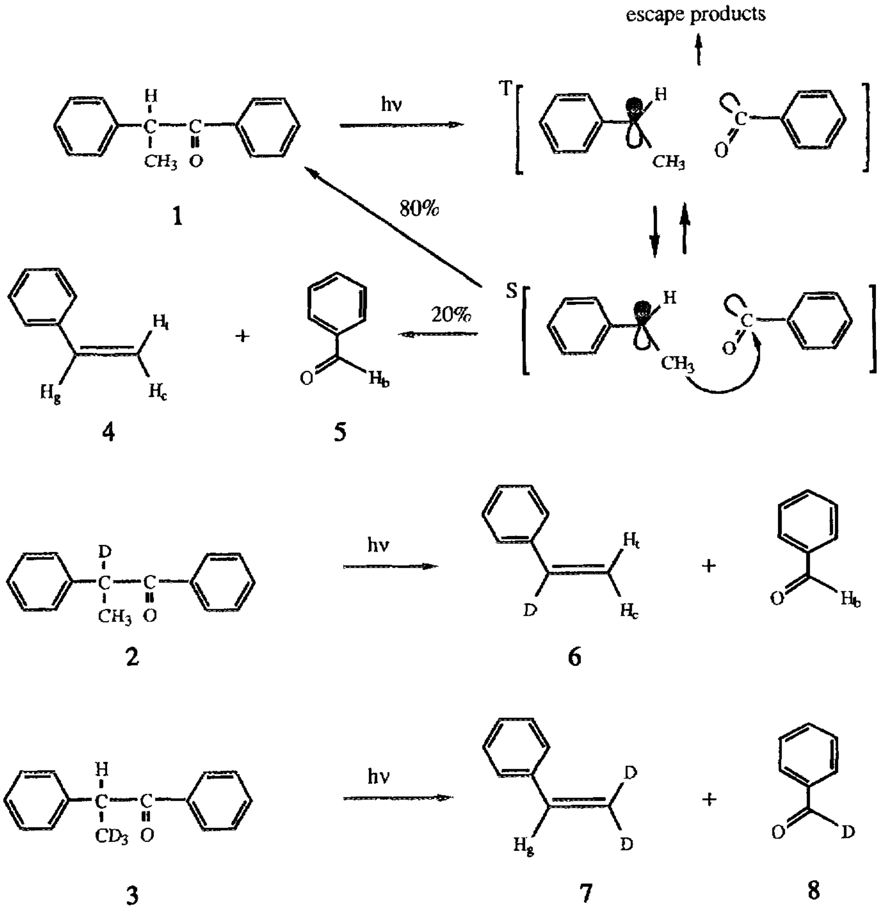

FIG. 3. Photolysis of α-methyldeoxybenzoin (**1**) and deuterated derivatives (**2**, **3**) in SDS micelles.

Cross relaxation. Effects of cross relaxation in high-field CIDNP have been studied by Closs *et al.* (*3, 14*). In high field, nuclear relaxation is quite slow ($\sim 0.1\ s^{-1}$) and manifests itself through changes in the relative intensities of spectral lines belonging to a given multiplet. These changes may be eliminated with $\pi/2$ pulses. Furthermore, redistribution of polarization is usually observed >10 s after the completion of the reaction (*3*). However, in low field, cross relaxation is fast and may substantially affect nuclear polarization on the time scale of sample transfer.

Let us consider the effect of cross relaxation in the AB system. This relaxation causes mixing of spin states correlating with the high-field states $|2\rangle$ and $|3\rangle$. It may be included in Eq. [3] by a nonunity coefficient $\xi = \exp\{-\int_0^T dt W(H)\}$, where $W(H)$ is the relaxation rate in the field $H = H(t)$. As Eq. [3] demonstrates, in low field (where $\Delta\nu < J$), the cross relaxation would not change polarization transferred nonadiabatically. However, it destroys adiabatically transferred polarization. Thus, effects of cross relaxation are similar to these of nonadiabatic transfer. Arguably, the same may be stated about more complex spin systems.

EXPERIMENTAL

The above examination suggests strong effects of the sample transfer on spin evolution in the nuclear systems. The most striking effect of this transfer is a violation of equivalency in the protons magnetically equivalent in the radical. Decoupling of these protons yields polarizations undistorted by the transfer. Perfect decoupling may be obtained with deutero substitution of all the protons in a product except the chosen one. The second-to-best decoupling may be achieved if the ex-equivalent protons belong to different products (however, they may be coupled to other protons). We tried both these strategies in our study on low-field CIDNP in disproportionation of phenacyl and *sec*-phenethyl radicals formed under photolysis of α-methyldeoxybenzoin and its deuterated analogs (**1**–**3**). In order to improve signal-to-noise ratio, these experiments were carried out with micellar aqueous sodium dodecyl sulfate (SDS) solutions. Trapping of the radicals inside micellar cages dramatically increases yield of disproportionation [from $<2\%$ in benzene to $\sim 18\%$ in SDS (*15–17*)]. This reaction occurs only in the geminate pairs (*17*). As a result, the photosystem yields ex-

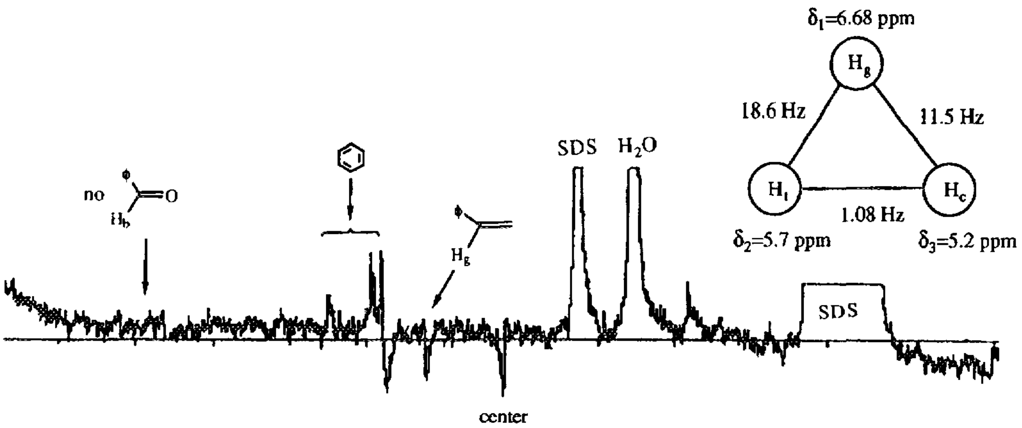

FIG. 4. NMR spectrum (100 MHz) obtained for photolysis of **3** in aqueous micellar SDS solution at H_{lab} = 10 mT. The signal from the *gem*-proton is in emission. The spectrum was obtained with a single $\pi/2$ RF pulse and no spinning of the sample.

tremely strong polarization in protons of benzaldehyde (**5**) and styrene (**4**; Fig. 3). It is also important that spin dynamics in the given pair were studied with a variety of techniques (*13*, *18–20*) which allows a reliable calculation of polarizations generated prior to the transfer.

Chemical shifts and spin–spin coupling constants in nonaromatic protons of styrene are reported in Fig. 4 (*21*). The *gem*-proton (H_g) has the highest shift, the *cis*-proton (in the conventional NMR notations, H_c) has the lowest one, and the *trans*-proton(H_t) has an intermediate one. These three protons are strongly coupled; however, *trans*- and *cis*-protons are weakly coupled ($J_{tc} \sim 1.08$ Hz). The α-proton in benzaldehyde (H_b) is weakly coupled to the aromatic ones; we may assume that the proton is isolated. Thus, the polarization of this nucleus cannot be affected by the sample transfer. The same may be concluded about *gem*-protons in the dideuterated styrene (**7**). In the monodeuterated styrene (**6**), *cis*- and *trans*-protons compose a weakly coupled AB system. Note that *cis*-, *trans*-, and benzaldehyde protons are all from the methyl group of *sec*-phenethyl radical and are magnetically equivalent in that radical. Thus, the systems give a good opportunity to study effects of violation in equivalency.

Ketones **1–3** were synthesized according to Ref. (*20*). Solutions (1 g/liter) of these ketones in 0.1 *M* micellar solution of SDS in D_2O were used. Solutions were prepared by stirring the crystalline ketones with micellar solution for two to five hours and were purged with helium for one hour prior to the measurement. The setup for observation of low-field CIDNP is reported in Ref. (*5*). Under constant pressure of helium, the solution flows from the vessel to a cylindrical quartz cell (Ø2 × 10 mm) where the sample is photolyzed for 0.5–1 s with a XeCl excimer laser (Lambda Physik, 308 nm, 150 mJ/pulse, 10 Hz) in the field of a homebuilt electromagnet (0–60 mT). In the course of the measurement, the field H_{lab} was gradually stepped; H_{lab} was controlled with a Hall probe magnetometer. The residual magnetization in the iron core of the magnet was carefully eliminated prior to every measurement in low field. The sample was transferred in the flow to the cavity of a 100 MHz Varian XL-100 spectrometer; the time τ of this transfer was <1 s. NMR spectra were obtained with a single $\pi/2$ pulse without spinning of the sample. Usually, this sequence was repeated 5–10 times for every field and the spectra were collected and averaged. A typical ^1H NMR spectrum obtained under these conditions is shown in Fig. 4. In the micellar solution, the signals from methyl protons of **1** and **2** are masked by a strong and broad signal from the aliphatic protons of SDS. Resonance lines of protons of styrene and benzaldehyde are sufficiently remote from this signal and are well resolved. No signals from benzaldehyde protons were found in the photolysis of **3**. This finding is in a good agreement with previous data on GC–MS, which indicates that geminate disproportionation involves only β-protons of substituted benzyl radicals (*16*).

To obtain the field dependences shown in Figs. 5 and 6, integrals of the resonance lines were plotted against the laboratory field. Polarizations of protons in styrene were found to be particularly difficult to reproduce in fields less than 0.2–0.3 mT. Depending on the flow rate and the repetition rate of the laser, we obtained either zero polarization of all three protons in styrene or nonzero polarizations for *cis*- and *gem*-protons. In relatively strong fields (>0.5 mT), the field dependences were well reproduced and did not vary with changes in the flow. Interestingly, we observed field-dependent polarized signals from admixtures of H_2O in D_2O in the photolysis of **1** and **2**. In contrast, this signal was found to be field-independent under photolysis of **3**. The field dependence of this proton was very similar to that of benzaldehyde proton after the subtraction of Boltzmann (dark-period) polarization. The GC–MS data suggest that H/D exchange of the aldehyde α-hydrogen with water is a very slow process (*16*). Presumably, the polarization was trans-

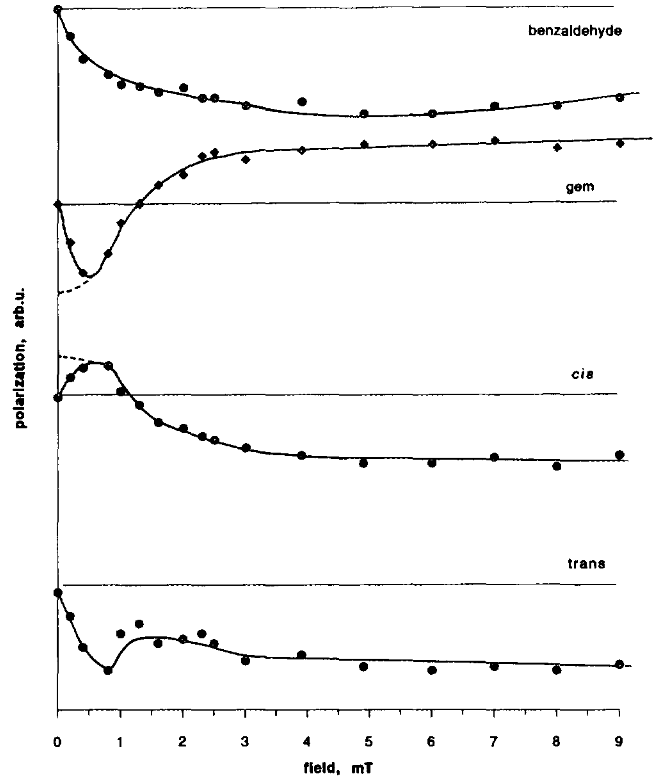

FIG. 5. Field dependences of polarization in nonaromatic protons of 4 and 5 obtained in laser photolysis of 1. Dashed lines show the polarization pattern obtained with a slow flow rate.

ferred to the hydrating water molecules via rapid cross relaxation (*22*).

RESULTS

In full accordance with our theoretical consideration, photolysis of 1 yielded qualitatively different field dependences of polarization in (magnetically equivalent in the radical) *cis, trans-*, and benzaldehyde protons (Fig. 5). At $H_{\mathrm{lab}} > 1.5$ mT, all these protons were in emission while the *gem*-proton was in absorption. In the very low field (<1.5 mT), the *cis*-proton was in absorption and the *gem*-proton was in emission. Although *trans*-protons and benzaldehyde protons were both in emission, their field dependences were not identical.

When ketone 3 was photolysed, the signal from *gem*-protons was in emission, with the field dependences resembling that of the benzaldehyde proton in photolysis of 1 and 2. Photolysis of 2 yielded fairly similar field dependences in *cis-*, *trans-*, and benzaldehyde protons. Clearly, the decoupling of protons in styrene restored equivalency in the polarizations of protons derived from β-hydrogens of the *sec*-phenethyl radical.

These results may be readily rationalized in terms of the transfer effects. The isolated proton in 5 and the *gem*-proton in 7 carried polarizations undistorted by the transfer. Because of very weak coupling of *cis-* and *trans*-protons in 6, it is unlikely that the transfer of the correspondent polarization is adiabatic. Consequently, these protons have nearly identical field dependences of polarization, which are similar to that of the benzaldehyde proton. In contrast, polarizations formed in the strongly coupled system of 4 were redistributed by the transfer. In zero field, adiabatically transferred polarizations in *gem-* and *cis*-protons are nonzero and opposite in sign, and that of the *trans*-proton is zero. This is in excellent agreement with the experiment. Moreover, with an increase in the transfer rate, adiabaticity of the transfer decreases and one may expect approach of all three polarizations to zero. This may explain the observed sensitivity to the flow and photolysis conditions.

DISCUSSION

Analysis of the ABC system in styrene indicates that there are two linear quasi-intersections of nuclear spin terms: the first one occurs at 40 mT (for terms correlating with $|\alpha\alpha\beta\rangle$ and $|\alpha\beta\alpha\rangle$) and has $Mv \approx 3.4$ T/s; the second one occurs at 75 mT and has $Mv \approx 2.9$ T/s. Assuming $v \sim 1\text{–}2$ T/s, we obtain $M \sim 1.5\text{–}3$. Thus, the transfer is more adiabatic than nonadiabatic. However, rapid cross relaxation would

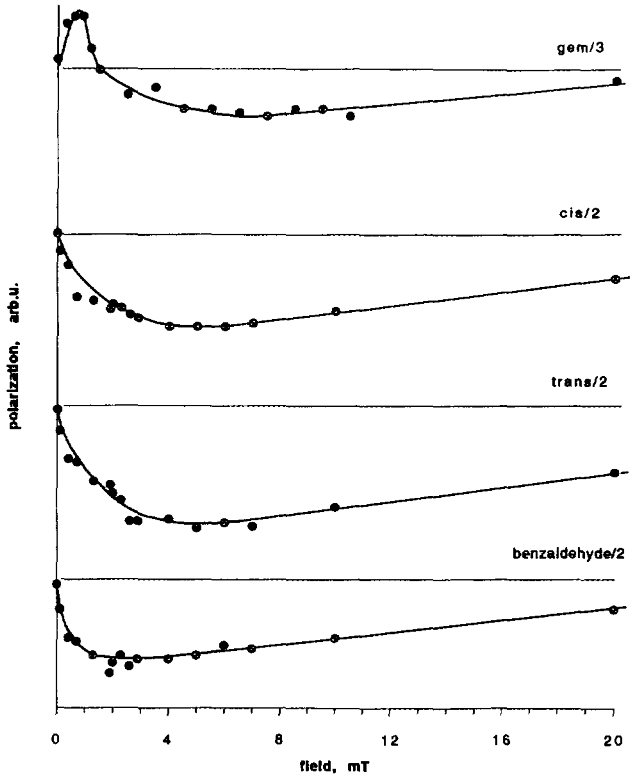

FIG. 6. Field dependences of polarization in nonaromatic protons of 6, 7, and 5 obtained in photolysis of 2 and 3.

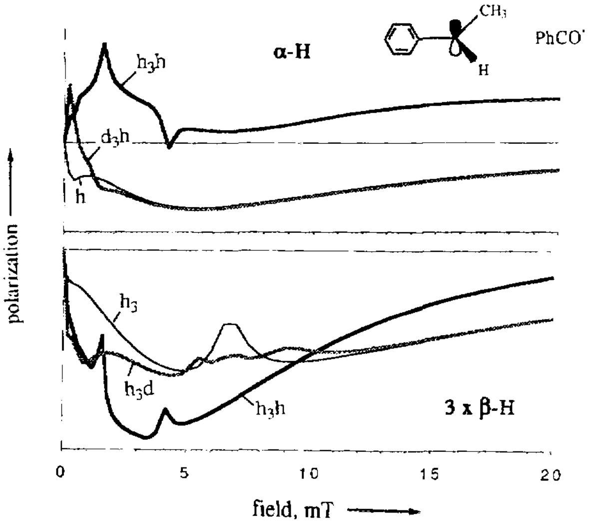

FIG. 7. Calculated field dependences of spin polarization in (decoupled) α-protons in **7** (photolysis of **3**; top) and β-protons in **6** and **5** (photolysis of **2**; bottom). For comparison, these polarizations are plotted together with spin polarizations in decoupled protons in **4** (photolysis of **1**) and hypothetic pairs in which A_α (or, respectively, A_β) is zero.

change the polarization pattern in such a way that it would resemble that formed upon nonadiabatic transfer.

Further insight into the transfer mechanism is impossible without knowledge of the polarizations formed in the laboratory field. Although deuteration decouples protons, it also changes their polarizations since the corresponding hfi coupling constants in the phenethyl radical become smaller. Thus, polarizations in the protons of **4** may be found only theoretically. We used the so-called supercage model of the micellized pairs developed in our previous work (*17, 23, 24*). In this model, the SDS micelle is represented as a spherical cavity of radius $R_m \approx 1.8$ nm with semitransparent walls. The fraction of radicals reflected back into the micelle at each encounter with the wall was estimated as 90–95% (*24*). Trapped radicals either react from the singlet state at each encounter or escape from the micelle (*24*). We assumed that the diffusion coefficient inside the micelles is approximately 7×10^{-6} cm^2/s (*24*). The model was successfully applied to the simulation of magnetic field (*17, 20*) and magnetic isotope effects (*20*), recombination kinetics (*25*), CIDNP (*23*), stimulated nuclear polarization (*5, 19*), and chemically induced dynamic electron polarization in micellized pairs.

Our calculation directly included distance-dependent electron-spin exchange $J(r)$ between the radicals. The exchange potential was approximated with an exponential function $J(r) = J_0 \exp[(R - r)/\lambda]$, with $J_0 \approx -10^{10}$ rad/s, $R = 0.6$ nm, and $\lambda \approx 0.05$ nm (*23, 24*). We also included the Zeeman interaction of *sec*-phenethyl ($g_1 = 2.0014$) and phenacyl ($g_2 = 2.0006$) radicals with the external field and hyperfine interactions of the first radical of α- and β-protons ($A_\alpha = -1.63$ mT and $A_\beta = +1.79$ mT) (*20*). Other hfi constants in this pair are less than 0.5 mT and were neglected. Solution of the master Liouville equation yielded ρ, the density matrix of the nuclear system in the singlet product of reaction. Diagonal elements of this matrix in the basis $|\sigma\rangle$ of eigenvectors of $\mathscr{H}_N$ in the laboratory field were considered as $\tilde{P}_\sigma$, and adiabatic and nonadiabatic polarizations were calculated. Results of this procedure are shown in Figs. 7 and 8.

This calculation satisfactorily reproduces field dependences of polarization in the decoupled systems of **6** and **7**. For example, it correctly predicts absorption/emission field dependences of polarization in the *gem*-proton in **7**. Note that emissive CIDNP for this proton results from flip-flop spin transitions in the region of avoided crossing of S and T-terms of the pair (*1*). If $J(r) = 0$, this polarization is positive. This example illustrates the significance of confinement of the radical partners inside the micellar body. Figure 8a shows what polarization would be observed in the protons of **4** if these protons were fully decoupled. In this case, *cis*-, *trans*-, and benzaldehyde protons would be in emission and

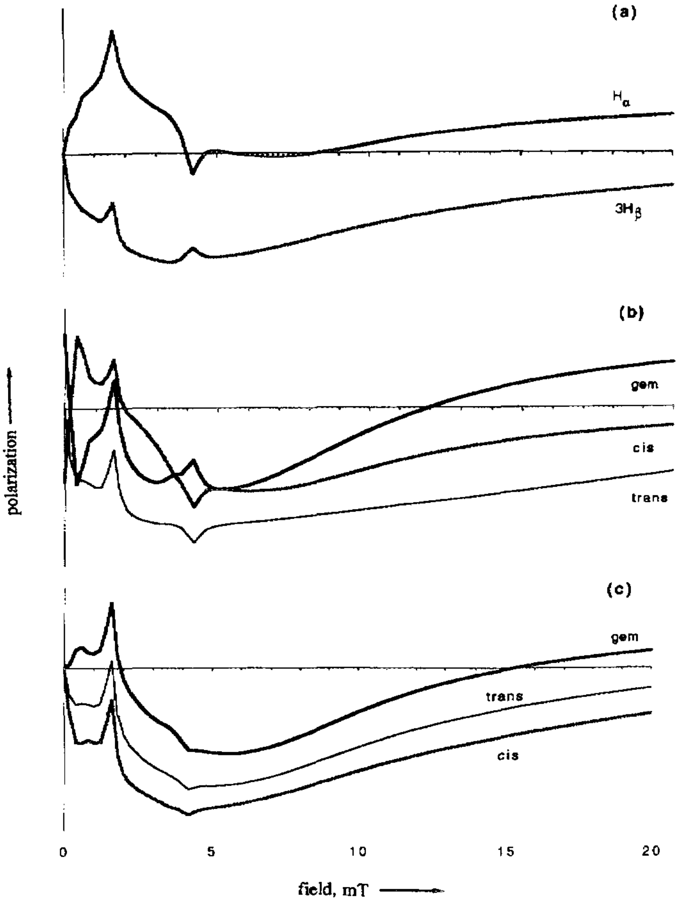

FIG. 8. Calculated field dependences of spin polarization in protons of **4** and **5** in photolysis of **1** (a) With no J coupling of the protons and polarization transferred (b) adiabatically and (c) nonadiabatically in the J-coupled ABC system of styrene.

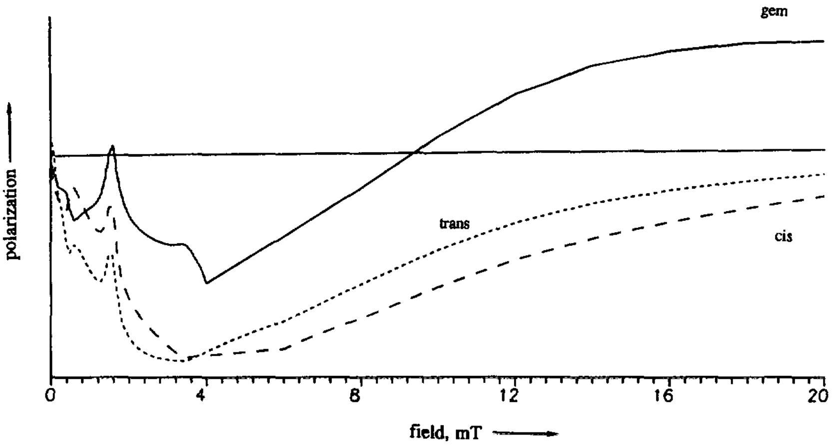

FIG. 9. Spin polarization of protons in **4** calculated with the master Liouville equation with linearly increasing $H(t)$ at $\tau = 1$ s.

the *gem*-proton would be in absorption. A change in the phase of polarization of the *gem*-proton in **4** (relative to **7**) is due to a quantum interference of flip-flop transitions in the two sets of magnetically equivalent nuclei with opposite signs of their hfi constants. This rare effect has already been observed and discussed in Ref. (*2*). Our calculation indicates that a decrease in the lifespan of the pair would change polarization in the *gem*-proton to emission. Plots shown in Fig. 8a satisfactorily reproduce polarizations in *gem*- and benzaldehyde protons at $H_{\mathrm{lab}} > 3$ mT.

Figures 8b and 8c illustrate redistribution of nuclear polarization as a result of purely adiabatic (Fig. 8b) and purely nonadiabatic (Fig. 8c) transfers. Not unexpectedly, none of these calculations fully reproduces the observed features. However, it is evident from Fig. 8c that the experimental transfer is not purely nonadiabatic. On the other hand, the model with purely adiabatic transfer gave polarization curves resembling those shown in Fig. 5. For example, the model gave absorption for *cis*-protons in very low field and emission in higher field. The opposite pattern was obtained for *gem*-protons, while *trans*-protons were in emission.

The inability of these models to reproduce experimental curves quantitatively partly originated in nonadiabaticity of the transfer for some spin terms. We tried to improve our model by simulating these effects. For simplicity it was assumed that the increase in the field $H(t)$ during the transfer is linear, $H(t) = H_{\mathrm{sp}}(t)/\tau$ at $t < \tau$ and $H(t) = H_{\mathrm{sp}}$ at $t > \tau$. In the absence of relaxation, the evolution of the spin system is given by the equation $d\rho(t)/dt = i[\rho(t), \mathcal{H}_{\mathrm{N}}(t)]$. It may be solved numerically. In these calculations $\rho(t)$ oscillates with time. To reduce uncertainty in the results, we integrated $\rho(t)$ within 0.5 seconds after the completion of the transfer at $t = \tau$. This procedure is quite justified since different portions of the photolysed solution arrive at the resonator with different delay times. A result of such a computation with $\tau = 1$ s is presented in Fig. 9. It shows the significance of nonadiabatic transfers in the regions of avoided crossing. Better agreement could probably be obtained if aromatic protons and spin relaxation were included.

CONCLUSION

Sample transfer is an unavoidable step in the observation of low-field CIDNP. This transfer changes polarizations in coupled nuclei and creates new coherences in the spin systems. Particularly, adiabatic transfer causes the so-called zero-field multiplet effect which (in contrast to the convenient multiplet effect) cannot be eliminated from NMR spectra with $\pi/2$ pulses. Both adiabatic and nonadiabatic transfer violate equivalency in polarization of protons which were magnetically equivalent in the radicals. Our experiments suggest that the effect should not be overlooked when CIDNP observations are performed on *J*-coupled nuclear systems in very weak magnetic fields. This result brings up serious questions as to the correctness of many previous works on low-field CIDNP.

APPENDIX

$$\begin{aligned}\mathrm{sgn}(L_a) = \mathrm{sgn}\{&2(A_a + A_b + A_c)\\ &\times [J_{ab}^2 + J_{bc}^2 + J_{ca}^2 - J_{ab}J_{bc} - J_{bc}J_{ca} - J_{ca}J_{ab}]^{1/2}\\ &+ (2J_{ab} - J_{bc} - J_{ca})(2A_aA_b - A_bA_c - A_cA_a)\\ &+ 3(J_{bc} - J_{ca})(A_bA_c - A_cA_a)\}\\ &\times \mathrm{sgn}(J_{ab}J_{bc} + J_{bc}J_{ca} + J_{ca}J_{ab}). \qquad [\mathrm{A1}]\end{aligned}$$

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REFERENCES

1. U. E. Steiner and T. Ulrich, *Chem. Rev.* **89,** 51 (1989).
2. K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, and A. L. Buchachenko, "Spin Polarization and Magnetic Effects in Radical Reactions," Elsevier, Amsterdam, 1984.
3. G. L. Closs, *in* "Chemically Induced Magnetic Polarization" (A. R. Lepley and G. L. Closs, Ed.), p. 95, Wiley, New York, 1973.
4. A. L. Buchachenko, "Chemical Polarization of Electrons and Nuclei," Nauka, Moscow, 1974. [In Russian]
5. E. G. Bagryanskaya and R. Z. Sagdeev, *Prog. React. Kinetics* **18,** 63 (1993).
6. A. D. Trifunac, R. G. Lawler, D. M. Bartels, and M. C. Thurnauer, *Prog. React. Kinetics* **14,** 43 (1986).
7. J.-K. Vollenweider and H. Fischer, *Chem. Phys.* **108,** 365 (1986).
8. R. Hany, J.-K. Vollenweider, and H. Fischer, *Chem. Phys. Lett.* **120,** 169 (1988).
9. A. Messiah, "Quantum Mechanics," Vol. 2, North-Holland, New York, 1961.
10. R. Kaptein, Ph.D. thesis, Leiden, 1971.
11. S. H. Glarum, *in* "Chemically Induced Magnetic Polarization" (A. R. Lepley and G. L. Closs, Ed.), p. 1, Wiley, New York, 1973.
12. H. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *J. Am. Chem. Soc.* **91,** 4228 (1969).
13. I. A. Shkrob, *Chem. Phys. Lett.* **210,** 432 (1993).
14. K. Müller and G. L. Closs, *J. Am. Chem. Soc.* **94,** 1002 (1972).
15. H.-G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *J. Org. Chem.* **39,** 691 (1974).
16. N. J. Turro and J. Mattay, *J. Am. Chem. Soc.* **103,** 4200 (1981).
17. V. F. Tarasov, I. A. Shkrob, E. N. Step, and A. L. Buchachenko, *Chem. Phys.* **135,** 391 (1989).
18. I. R. Gould, M. B. Zimmt, N. J. Turro, B. H. Baretz, and G. F. Lehr, *J. Am. Chem. Soc.* **107,** 4607 (1985).
19. E. G. Bagryanskaya, Yu. A. Grishin, R. Z. Sagdeev, V. F. Tarasov, I. A. Shkrob, and A. L. Buchachenko, *Khim. Fiz.* **10,** 1365 (1991).
20. I. A. Shkrob, V. F. Tarasov, and A. L. Buchachenko, *Chem. Phys.* **153,** 443 (1991).
21. W. Brügel, "Handbook of NMR Spectral Parameters," p. 350, Vol. 2, Heyden, 1979.
22. K.-G. Seifert and J. Bargon, *Angew. Chem.* **85,** 763 (1973); *Ber. Bunsenges. Phys. Chem.* **78,** 187 (1974).
23. I. A. Shkrob, V. F. Tarasov, and E. G. Bagryanskaya, *Chem. Phys.* **153,** 427 (1991).
24. V. F. Tarasov, N. D. Ghatlia, A. L. Buchachenko, and N. J. Turro, *J. Am. Chem. Soc.* **114,** 9517 (1992).
25. I. A. Shkrob and V. F. Tarasov, *Chem. Phys.* **147,** 369 (1990).